INVESTIGATION IN THE FIELD OF DIACETYLENE DERIVATIVES COMMUNICATION 17. SPECTRAL INVESTIGATION OF THE MUTUAL INFLUENCE OF HETEROATOMS AND MULTIPLE BONDS IN ENYNE SYSTEMS

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The different ability of oxygen, sulfur, and nitrogen atoms to interact with an unsaturated system of electron pairs has already been noted [1, 2]; this is the cause of the change in reactivity in the series of ethylvinyl ethers, thioethers, and amines, for example, in reactions of hydration [3-5] or the addition of carbonyl compounds [6]. Continuing a systematic study of the relationship between the structure and reactivity in the series of ethylvinyl compounds of the type of $R_1C \equiv C - CH = CHXR_2$, where X = O, S or N; R_1 and R_2 are organic radicals, we conducted a spectral investigation and made an attempt to determine the principles in their reactivity on the basis of the concept of the displacement of electron density under the influence of O, S, and N atoms. For this purpose we took the IR and UV spectra of the investigated compounds, measured the integral intensities of the acetylenic and ethylenic bonds, as well as the dipole moments for some of them. The results are presented in Table 1.

In the investigated ethylvinyl compounds, the vibration frequency of the triple bond lies within the range 2208-2230 cm⁻¹ in the case of disubstituted compounds (V)-(X) and 2078-2096 cm⁻¹ for monosubstituted (II), (III), and (IV). These values agree with the data of other authors [7], who investigated viny-lacetylene compounds with alkyl substituents. Evidently, the introduction of a heteroatom into the γ -position with respect to the acetylene bond has no appreciable influence on the vibration frequency of the latter. At the same time, the values of the vibration frequencies of the ethylenic bond differ substantially depending



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Compound							
no.	formula	vc <u>≕</u> c	Ac≡c	^C==C	AC=C	λ,nm (ε)	·μ, D
I	$CH_{s}=CH-C\equiv C-C (OH) CH_{s}$	2210	0,005	1612	0,120	222 (13500) 232 (11400)	_
11	(C ₁ H ₄) ₂ NCH=CH−C≡CH	2078	0,660	1620	2,900	278 (14300) 318 (6000)	2,87
111	C ₂ H ₅ OCH=CH-C=CH	2096	0,170	1638	0,580	236 (13100)	2,36
IV	C ₂ H ₆ SCH=CH-C=CH	2094	0,063	1560	0,056	276 (12500)	2,16
v	$(C_2H_b)_2$ NCH=CHC=C-C (CH ₃) ₂	2195	0,520	1623	1,490	284 (14500)	-
VI	OH C₄H₄OCH=CHC≡CC (CH₃)₂ OH	2210	0,130	1636	0,320	240 (14200)	_
VII	$ C_{2}H_{5}SCH = CH - C = C - C (CH_{3})_{2} $	2208	0,035	1560	0,015	273 (14000)	3,05
VIII	OH CH ₃ OCH=CH-C≡C-	2210	0,130	1636	0,340	240 (14400)	2,97
IX	OH C ₂ H ₆ SCH=CH-C=C	2208	0,043	1560	0,014	278 (14100)	2,81
х	C₂H₅SCH=CHC≡C−C≡C− OH	2213 2132	0,260 0,120	1558	0,180	224 (8600) 236 (6000) 298 (14000) 310 (16100)	

TABLE 1. Spectral Characteristics and Dipole Moments of Ethylvinyl Compounds

on the nature of the heteroatom in the α -position to the C=C bond. Although the frequency of the C=C bond in the compound (I) is 1612 cm⁻¹, when an oxygen atom is introduced into compounds (III), (VI), and (VIII), it fluctuates within the range 1636-1645 cm⁻¹. In the case when X=N [Compounds (II), (V)], $\nu_{C=C}$ 1620 cm⁻¹, while in the compounds (IV), (VII), (IX), and (X), where X=S, $\nu_{C=C}$ 1560 cm⁻¹. Such a change in frequency agrees with the concept of the influence of the inductive effects of the oxygen and nitrogen atoms. The more electronegative oxygen atom somewhat displaces the electron density in the enyne system in the direction of the heteroatom. The conjugation existing there is disturbed, and the polarity is decreased. This leads to an increase in the vibration frequency of the ethylenic bond to ~1640 cm⁻¹ in comparison with vinylacetylene. The lower value of $\nu_{C=C}$ in the case of the nitrogen atom is explained by the competitive influence of the more mobile unshared electron pairs than those of oxygen.

The substantial decrease in the vibration frequency of the C = C bond in sulfur-containing compounds (IV), (VII), (IX), and (X) might have been explained by an increase in the conjugation on account of the sulfur atom, which plays the role of an electron donor. However, this is contradicted by the decrease in the intensity of the bands of the multiple bonds, almost tenfold in comparison with O- and N-containing viny-lacetylene compounds. The determining factor in the change in the vibrations may be the effect of the masses and certain peculiarities of the electronic structure of the sulfur atom. Thus, our earlier conclusion [1] that the influence of the heteroatoms is exerted chiefly on the vibrations of the double bond, without introducing any significant changes into the vibrations of the triple bond, is confirmed.

More complete information on the changes in the electron density of the molecules was obtained in a consideration of the values of the integral intensities. In the vinylacetylene molecule, in which all the carbon atoms lie in one place, the electrons forming the π -cloud of the multiple bonds can be polarized to some degree. This leads to the formation of molecular orbitals encompassing all the carbon atoms, as a result of which there is an increase in the length of the multiple bonds and an increase in the intensity. The largest value of the intensity of the acetylenic and ethylenic bonds was obtained in compounds (II) and (V) (X=N), the smallest in (IV), (VII), and (IX) (X=S). The unshared pairs of electrons of the nitrogen atom, entering into conjugation with the enyne system, increase the intensity of the multiple bonds. In this case the shift of electron density is directed toward the acetylenic bond, which is confirmed by the electronic polarization, which can be assumed on the basis of the value of the dipole moment (2.87 D). The reduction of the intensity of the absorption bands of the multiple bonds in the case of X=S can be explained if we consider that sulfur, in contrast to oxygen and nitrogen, has not only six valence s- and p-electrons in its valence shell (M), but also vacant d-orbitals, capable of accepting excited electrons. The C-S bond partially acquires double-bonded properties, while the d-electron wave functions of the sulfur atom can overlap the electron clouds of the π -electrons of the multiple bond in the vinyl position, thereby limiting their mobility. The acceptor capacity of sulfur on account of the presence of vacant dorbitals, the filling of which promotes a large separation of charges, is higher than that of oxygen, despite the lower electronegativity of the S atom. This may also lead to a displacement of the polarization in the enyne system in the direction of the heteroatom. The value of the dipole moment (2.16 D) agrees with our hypothesis. In compound (X), where X=S, the chain of conjugation is enlarged on account of the introduction of a second acetylene bond, and the intensity increases almost tenfold in comparison with compounds (IV) and (VII).

In an investigation of the PMR spectra of ethylvinyl ethers and their sulfur and nitrogen-containing analogs on the basis of the values of the chemical shifts, the same electronic displacements were established [2]. The influence of the heteroatom on the electronic structure of the molecule can be reduced to two effects: the π -electronic conjugation, i.e., a displacement of electron density from the heteroatom toward the double and triple bonds, and the σ -inductive effect, leading to an attraction of electrons to the heteroatom.

In the UV absorption spectra, the band with maximum at 219-230 nm pertains to an electronic transition of the $\pi - \pi^*$ type. In oxygen-containing compounds (II), (VI), and (VIII), bands with a maximum at 233-240 nm correspond to this transition. When nitrogen and sulfur are introduced, a bathochromic shift of the band by 30 nm is observed. An increase in the conjugation on account of the introduction of a second acetylenic bond [compound (X)] produces the appearance of several bonds in the electronic spectrum (Fig. 1).

EXPERIMENTAL

Compounds (II)-(IV) were produced by the reaction of diacetylene with diethylamine [8], ethanol [3], and ethylmercaptan [9]. 1-(N, N-Diethylamino)-5-methylhexene-1-yne-3-ol-5 (V), bp $105-107^{\circ}$ (2 mm); n_D^{20} 1.5240, was synthesized by the condensation of the Li derivative of N, N-diethylaminobutene-1-yne-3 with acetone in a solution of tetrahydrofuran at 0°. Alkoxy- and alkylthioenyne alcohols (VI)-(IX) were produced according to the procedure of [6], while an alkylthioenediyne alcohol (X) was produced according to the procedure of [6], while an alkylthioenediyne alcohol (X) was produced according to the procedure of [10]. The IR spectra in CC14 solution were obtained on a UR-10 spectrophotometer; the integral intensity (A·10⁴, cm⁻²·mole⁻¹·liter) was calculated according to the method of [11]. The accuracy of the determination of the intensity was 10%. The UV spectra were taken in ethanol solution on an SF-4A spectrophotometer. The dipole moment was determined by measuring the dielectric permeability and calculation according to the Debye formula.

CONCLUSIONS

1. The IR and UV spectra were obtained, and the integral intensities of acetylenic and ethylenic bonds in ethylvinyl ethers, thioethers, and amines were measured.

2. The influence of the heteroatom is exerted chiefly on the vibration frequencies of the ethylenic bond.

3. From the values obtained for the integral intensities, it follows that the influence of the heteroatom on the electronic structure of the molecule is reduced to two effects: to π -electronic conjugation and the σ -inductive effect.

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